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Defects in Photovoltaic Materials and the Origins of Failure to Dope Them

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DEFECTS IN PHOTOVOLTAIC MATERIALS AND THE ORIGIN OF FAILURE TO DOPE THEM

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ABSTRACT

I will review the basic physical principles underlying the formation energy of various intrinsic defects in common photovoltaic materials. I then use the above principles to explain why doping of semiconductors is, in general, limited and which design principles can be used to circumvent such limits. This work can help design strategies of doping absorber materials as well as explain how TCOs work. Recent results on the surprising stability of *polar* (112) + $(\bar{1}\,\bar{1}\,\bar{2})$ surfaces of CIS will also be described in this context.

Conditions for n-type doping:

(i) *Donors must have shallow levels so they are readily ionizable*.

But which defects lead to shallow levels? For ZnO candidates are V_O, or Zn_i, or Zn_O. Our calculations [1] show that Zn_i has indeed a shallow level (while V_O is deep). For SnO_2 [2], V_O is shallow, as is Sn_i. This is seen in Fig. 1, which depicts the formation energies of various defects in SnO_2. Note that Sn_i has donor levels *inside* the conduction band. Surprisingly, we find that hydrogen impurity also forms a shallow donor in these materials, which can also lead to n-typeness. This is seen in Fig. 2. Again, the donor level is inside the conduction band.

(ii) *Donors must have a low formation enthalpy so that the concentration of donors is high*.

For ZnO we find that this holds for Zn_i that is easily formed, whereas in SnO_2 this holds for Sn_i. This is seen in Fig. 1, showing Sn_i has the lowest ΔH.

(iii) *Electron-killer centers must have high formation enthalpy, so their concentration is low*.

This could mean that O_i, V_{Zn} (in ZnO) or V_{Sn} (in SnO_2) have high formation enthalpy. Our calculations show that this is the case for ZnO and SnO_2: Fig. 1 shows that V_{Sn} and O_i are high-energy defects in SnO_2.

We see that ZnO and SnO_2 are predicted to be easily n-dopable via intrinsic defects, and H impurities. The reason that n-type doping is limited in $CuGaSe_2$ is the failure to fulfill condition (iii). This situation is summarized via the "phenomenological doping-limit rule."

The "doping limit rule" for n-type doping [3]:

"A material cannot be doped successfully n-type if its Conduction Band Minimum (CBM) is too close to vacuum (i.e., its electron affinity is too small)." This is the case for diamond, AlN, $CuGaSe_2$, etc. In these cases, electron-killer defects such as cation-vacancy will form and compensate the electron-producing agent. Conversely, a material can be doped successfully n-type if its CBM is as far away from vacuum as possible (large electron affinity). This is the case in ZnO, SnO_2, InP, etc.

Design Principles: One can enhance n-type dopability by lowering the CBM, e.g., via N-alloying of III-V's or oxygen alloying in II-VI's. Any lowering of the CBM, further away from vacuum will help.

Conditions for p-type doping:

(i) *Acceptors must have shallow levels so they are readily ionizable*.

For ZnO [1] candidates could include O_i and V_{Zn}, while for SnO_2 they could be O_i and V_{Sn}. Our calculation (Fig. 1) shows that for SnO_2 there are no shallow acceptors.

(ii) *Acceptors must have low formation enthalpy so that the concentration of acceptors is high*.

Our calculation shows that for ZnO this is true only for O-rich but not for Zn-rich conditions.

(iii) *Hole-killers must have high formation enthalpy so that they do not form*.

For ZnO this could include V_O, Zn_i or Zn_O. Our calculation shows that his condition is *not* met for ZnO where the hole-killer V_O and Zn_i are easily formed. This is the reason why ZnO cannot be easily doped (at least in equilibrium) p-type.

The doping limit rule for p-type doping:

The situation can be summarized again by the phenomenological doping-limit rule: "A material cannot be doped p-type if its VBM is too far from the vacuum level (intrinsic work-function is too big)." This is the case for common oxides such as ZnO, MgO, CaO, etc. In this case, hole-killers such as cation

interstitials or anion vacancies can form readily, thus compensating hole formation. Conversely, a material can be doped p-type if its VBM is high in energy (small intrinsic work function).

Design principles: p-type dopability can be enhanced by adding a d-band metal (e.g., Cu), since the d-states repel upwards the anion p-states that form the VBM. Thus, $CuB^{III}X_2^{VI}$ compounds are easier to make p-type than II-VI's. Also, Telluride's (in II-VI's) and antimonides (in III-V's) have a high VBM energy, and thus are easily made p-type.

Doping Oxides:

Stannic oxide (SnO_2) is a prototype "transparent conductor," exhibiting the seemingly contradictory properties of high metallic conductivity with nearly complete transparency in the visible range. First-principles calculations are employed to determine the conditions required for this unusual effect by investigating the role of intrinsic defects and hydrogen impurity. It is found that the tin interstitial and oxygen vacancy predominate in the defect structure of SnO_2 due to their low formation energies and attractive interaction between them. These intrinsic defects donate conduction electrons in undoped SnO_2 with almost no reduction in optical transparency. Moreover, hydrogen is found to act as an electron source in SnO_2.

We also find that (i) Sn_i has a very low formation energy in SnO_2 and will thus exist in large concentration. Furthermore, this off-stoichiometry-promoting defect also produces a donor level *inside* the conduction band, leading to instant ionization and conductivity. (ii) The reason for the stability of interstitial Sn in SnO_2 is the existence of *two* oxidation states of tin, i.e., Sn^{4+} (in SnO_2) and Sn^{2+} (in SnO). Thus, Sn_i can form in SnO_2 easily since it creates a local bonding environment that resembles that in stable SnO. (iii) The presence of Sn_i lowers dramatically the formation energy of V_O. This explains large oxygen deficiency. We explain (iv) the absence of spontaneous formation of acceptor "killer defects" and (v) the absence of inter conduction band absorption. Furthermore, (vi) despite the fact that H is expected to behave as an acceptor in an n-type material, the oxygen-bonded hydrogen in SnO_2 is found to enhance n-type conduction.

Hydrogen is a ubiquitous impurity in most semiconductors, including elemental (e.g., Si), compound (e.g., GaAs) and wide gap (e.g., III-V nitrides and II-VI's) semiconductors. In these systems, hydrogen is known to be *amphoteric*, forming an acceptor level in n-type and a donor level in p-type materials. In contrast, hydrogen can lead to electron conduction in some wide gap oxides such as SnO_2 and ZnO: it has been observed long ago that n-type conductivity of SnO_2 increases under H_2 atmoshphere; similar observations for ZnO have recently been attributed to H incorporation into n-type ZnO as a donor. These observations raise the question of what the basic systematic is at work here: if H can be incorporated into some materials, which one will be doped by H (i.e., become conductive) and which will not? Our first-principles study shows that SnO_2 and CdO can be doped n-type by hydrogen incorporation, whereas H in MgO yields a deep level inside the band gap, so MgO is not doped by hydrogen. Our results indicate that the distinction between H as an n-type dopant and as a non-doping impurity depends on whether the "hydrogen pinning level," estimated to be located approximately at 3.0 ± 0.4 eV below the vacuum level, is above the materials CBM (in which case H dopes it) or below the materials CBM (in which case H is non-doping). This is shown in Fig. 3. Generally, low-electron-affinity oxides (whose CBM is close to vacuum) will not be doped upon H incorporation. Likely examples include BaO, NiO, SrO, HfO_2 and Al_2O_3. High-electron-affinity oxides, however, will be doped upon H incorporation. Likely examples include Ag_2O, HgO, CuO, PbO, PtO, IrO_2, RuO_2, PbO_2, TiO_2, WO_3, Bi_2O_3, Cr_2O_3, Fe_2O_3, Sb_2O_3, Nb_2O_5, Ta_2O_5, $FeTiO_3$ and $PbTiO_3$.

The surface of CIS and it's doping [4]**:**

In zinc-blende semiconductors, the *nonpolar* (110) surface is stabler than all polar surfaces because the formation of the latter require the creation of charge-neutralizing but energetically costly surface reconstruction. Our first-principles calculations on $CuInSe_2$ reveal that in the double-zincblende (chalcopyrite) structure, (112)-cation plus $(\bar{1}\,\bar{1}\,\bar{2})$-anion *polar* facets are lower in energy than the unfaceted nonpolar (110) plane, despite the resulting increased surface area. We show that this effect results from the remarkable stability of surface defects (Cu-vacancy, Cu-on-In antisite) in chalcopyrites, and explains the hitherto puzzling formation of polar microfacets when one attempts to grow a nonpolar chalcopyrite surface.

We predict the polar surface to be stabilized by Cu-vacancies (V_{Cu}) in Cu poor conditions, and by Cu-on-In antisite defects Cu_{In} in In poor conditions. Our result might explain the dramatic reduction in free-carrier density observed when growing the nominally nonpolar chalcopyrite surface that reverts to (112) + $(\bar{1}\,\bar{1}\,\bar{2})$ polar micro facets: The conditions for electrostatic stability require the surface defects considered here to be fully ionized, since otherwise they would not accomplish the needed charge neutralization of the polar surfaces. In particular, the electrostatic potential pushes the valence band up until it overlaps the acceptor defects at the (112) surface, ionizing them and releasing holes. These holes, however, do not provide free carriers within the bulk of the sample, as they are confined electrostatically at or near the anion surface. If the latter also has an ordered-defect reconstruction

involving donors such as anion vacancies, these will exactly compensate the holes from the cation surface. In either case, the polar-faceted nonpolar plane is *autocompensated* by the equal areas of anion and cation facets leading to the observed dramatic decrease in carrier density. This compensation does not occur when the chalcopyrite (112) plane is grown alone.

Cluster doping:

We finally discuss the possibility of co-doping. Our total energy calculations for ZnSe co-doped with 2Ga+As or with Ga+2As reveal that co-doping is thermodynamically unstable. A new, surprising form of "cluster-doping" is, however, shown to be stable! Consider, for example the ZnSe crystal, doped by atoms of Ga and atoms of As. We can imagine a Ga-($As_{4-n}Se_n$) tetrahedron, embedded inside ZnSe. Conventional doping ("mono-doping") corresponds to n=4, i.e., Ga-replacing-Zn, leading to Ga-Se_4 unit inside ZnSe. Co-doping corresponds to n=2, i.e., 2As+Ga in ZnSe, resulting in the $GaAs_2Se_2$ unit. Finally, "cluster doping" corresponds to n=1 or n=0, namely $GaAs_3Se$ or $GaAs_4$ cluster inside ZnSe. We calculated the formation energies of all clusters $0 \leq n \leq 4$ and different charge states (Fig. 4). We find that monodoping and cluster-doping are stable in some ranges of chemical potential μ_{As} - μ_{Se}, but that co-doping is never stable. This could open a new strategy for overcoming doping bottlenecks.

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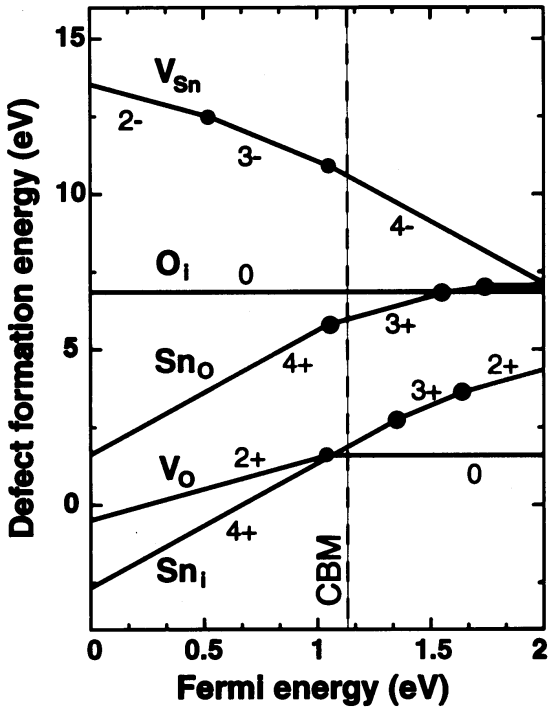

Fig. 1: Calculated formation energies for defects in SnO_2 vs. the position of the Fermi energy. Solid dots indicate transition levels from one charge state to the other.

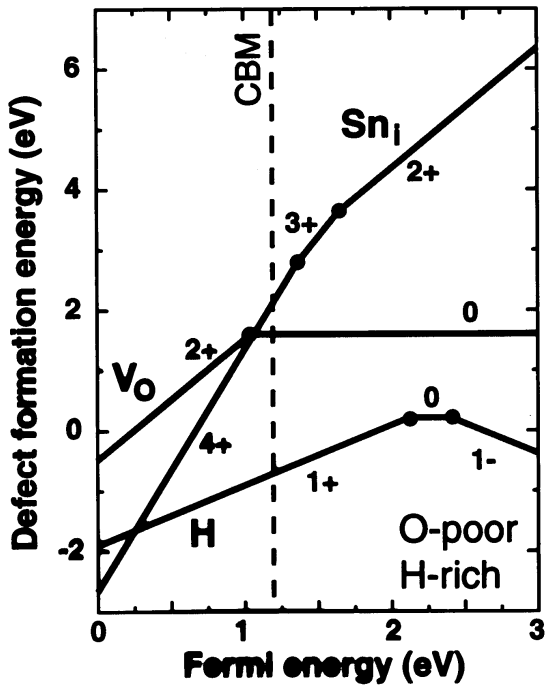

Fig. 2: Calculated formation energies of H in SnO_2.

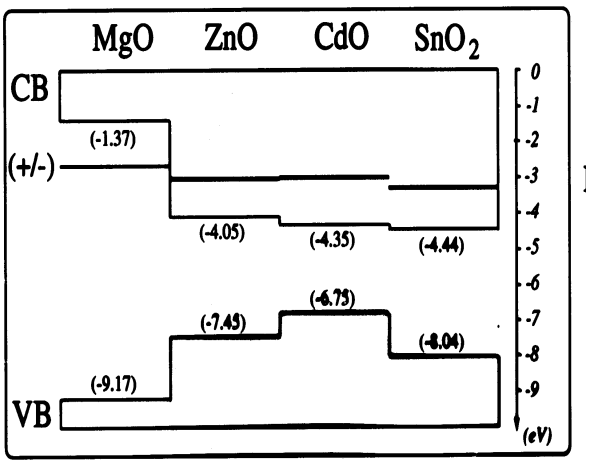

Fig. 3: Position of hydrogen pinning level (+/-). If a material has a CBM above this level (e.g., MgO), the incorporation of H will not make it conductive. Conversely, if a material has a CBM below this level (ZnO), then H incorporation will render it n-type.

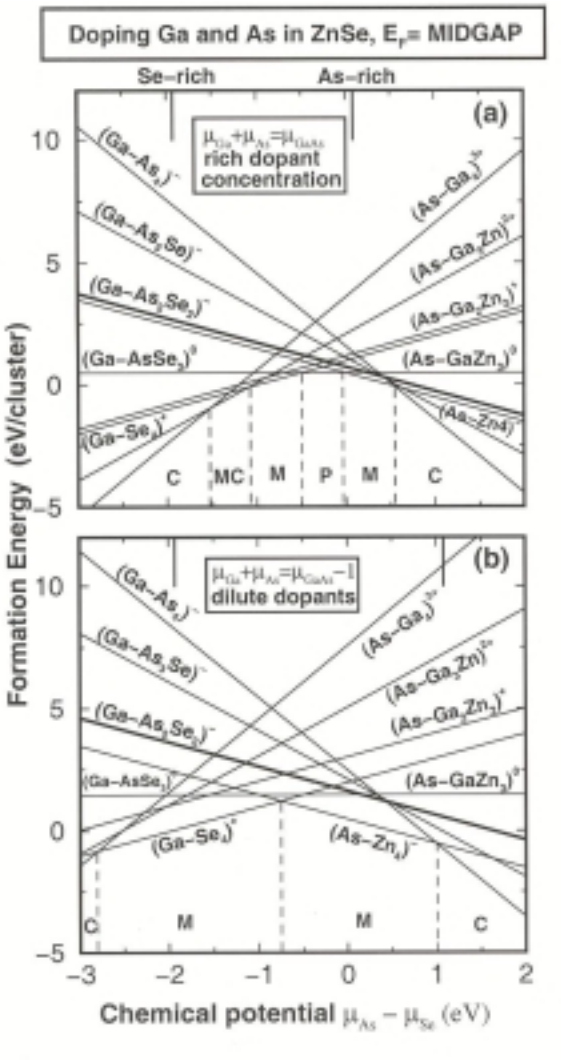

Fig. 4: Prediction of formation energies of various Ga ($As_{4-n}Se_n$) clusters in ZnSe. N=2 is co-doping (never stable), n=4 is monodoping (stable in some chemical potential range), whereas n=0 and n=1 is cluster doping. The latter is stable at the extreme chemical potential limits.

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